



Patent  
TS-1256 (US)  
JDA

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Jennifer D. Adamson

Date: February 2, 2004

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	)	
	)	
DAVID C. EUBANKS ET AL	)	
	)	
Filed August 26, 2003	)	Examiner:
	)	
Serial No. 10/648,072	)	Group Art Unit:
	)	
PREPARATION METHOD	)	February 2, 2004
	)	

COMMISSIONER FOR PATENTS  
P. O. Box 1450  
Alexandria, VA 22313-1450

Sir:

**CLAIM TO PRIORITY**

Applicant reaffirms the claim for the benefit of filing date of the following foreign patent application referred to in Applicant's Declaration:

EP Application Serial No. 02016086.7 - filed July 19, 2002

A copy of the application certified by the European Patent Office is enclosed.

Respectfully submitted,  
DAVID C. EUBANKS ET AL

By \_\_\_\_\_  
Attorney, Jennifer D. Adamson  
Registration No. 47,379  
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P. O. Box 2463  
Houston, Texas 77252-2463

Enclosure

**REGISTRY OF PATENTS  
SINGAPORE**

This is to certify that the annexed is a true copy of document filed for the following Singapore patent application.

Date of Filing : 27 AUGUST 2002

Application Number : 200205213-2

Applicant(s) /  
Proprietor(s) of  
Patent : SHELL INTERNATIONALE RESEARCH  
MAATSCHAPPIJ B.V.

Title of Invention : PREPARATION METHOD



SHARMAINE WU (Ms)

Assistant Registrar  
for REGISTRAR OF PATENTS



\*G00001\*

**PATENTS FORM 1**

Patents Act  
(Cap. 221)  
Patents Rules  
Rule 19

**INTELLECTUAL PROPERTY OFFICE OF SINGAPORE**

**REQUEST FOR THE GRANT OF A PATENT UNDER  
SECTION 25**



101101

\* denotes mandatory fields

**1. YOUR REFERENCE\***

1012917PAT/Shell/MK/FL

**2. TITLE OF  
INVENTION\***

PREPARATION METHOD

**3. DETAILS OF APPLICANT(S)\* (see note 3)**

Number of applicant(s)

1

(A) Name

**SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.**  
(a Netherlands company)

Address

Carel van Bylandtlaan 30, 2596 HR The Hague, The Netherlands.

State

Country

NL

☒

For corporate applicant



For individual applicant

State of incorporation

State of residency

Country of incorporation

NL

Country of residency



For others (please specify in the box provided below)

(B) Name

Address

State

Country



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☐ For corporate applicant

State of incorporation

☐ For individual applicant

State of residency

Country of incorporation

Country of residency

☐ For others (please specify in the box provided below)

(C) Name

Address

State

Country

☐ For corporate applicant

State of incorporation

☐ For individual applicant

State of residency

Country of incorporation

Country of residency

☐ For others (please specify in the box provided below)

☐

Further applicants are to be indicated on continuation sheet 1

4. DECLARATION OF PRIORITY (see note 5)

A. Country/country designated

File number

Filing Date

DD MM YYYY

B. Country/country designated

File number

Filing Date

DD MM YYYY

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Further details are to be indicated on continuation sheet 6

5. INVENTOR(S)\* (see note 6)

A. The applicant(s) is/are the sole/joint inventor(s)

Yes

☐

No

☒

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B. A statement on Patents Form 8 is/will be furnished

Yes

☒

No

☐

6. CLAIMING AN EARLIER FILING DATE UNDER (see note 7)

☐

section 20(3)

☐

section 26(6)

☐

section 47(4)

Patent application number

DD MM YYYY

Filing Date

Please mark with a cross in the relevant checkbox provided below  
(Note: Only one checkbox may be crossed.)

☐

Proceedings under rule 27(1)(a)

DD MM YYYY

Date on which the earlier application was amended

☐

Proceedings under rule 27(1)(b)

7. SECTION 14(4)(C) REQUIREMENTS (see note 8)

Invention has been displayed at an international exhibition. Yes

☐

No

☒

8. SECTION 114 REQUIREMENTS (see note 9)

The invention relates to and/or used a micro-organism deposited for the purposes of disclosure in accordance with section 114 with a depository authority under the Budapest Treaty.

Yes

☐

No

☒

9. CHECKLIST\*

(A) The application consists of the following number of sheets

i.	Request	<input type="text" value="5"/>	Sheets
ii.	Description	<input type="text" value="7"/>	Sheets
iii.	Claim(s)	<input type="text" value="2"/>	Sheets
iv.	Drawing(s)	<input type="text" value="-"/>	Sheets
v.	Abstract (Note: The figure of the drawing, if any, should accompany the abstract)	<input type="text" value="1"/>	Sheets
Total number of sheets		<input type="text" value="15"/>	Sheets

(B) The application as filed is accompanied by:

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Priority document(s)

☐

Translation of priority document(s)

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☒

Statement of inventorship  
& right to grant

☐

International exhibition certificate

10. DETAILS OF AGENT (see notes 10, 11 and 12)

Name

Donaldson & Burkinshaw

Firm

11. ADDRESS FOR SERVICE IN SINGAPORE\* (see note 10)

Block/Hse No.

Level No.

Unit No./PO Box

3667

Street Name

Building Name

Postal Code

905667

12. NAME, SIGNATURE AND DECLARATION (WHERE APPROPRIATE) OF APPLICANT OR AGENT\* (see note 12)

(Note: Please cross the box below where appropriate.)

☒

I, the undersigned, do hereby declare that I have been duly authorised to act as representative, for the purposes of this application, on behalf of the applicant(s) named in paragraph 3 herein.



Michael S. Kraal

Name and Signature

DD MM YYYY

27-08-2002

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## NOTES:

1. This form when completed, should be brought or sent to the Registry of Patents together with the rest of the application. Please note that the filing fee should be furnished within the period prescribed.
2. The relevant checkboxes as indicated in bold should be marked with a cross where applicable.
3. Enter the name and address of each applicant in the spaces provided in paragraph 3.  
Where the applicant is an individual
  - Names of individuals should be indicated in full and the surname or family name should be underlined.
  - The address of each individual should also be furnished in the space provided.
  - The checkbox for "For individual applicant" should be marked with a cross.  
Where the applicant is a body corporate
  - Bodies corporate should be designated by their corporate name and country of incorporation and, where appropriate, the state of incorporation within that country should be entered where provided.
  - The address of the body corporate should also be furnished in the space provided.
  - The checkbox for "For corporate applicant" should be marked with a cross.  
Where the applicant is a partnership
  - The details of all partners must be provided. The name of each partner should be indicated in full and the surname or family name should be underlined.
  - The address of each partner should also be furnished in the space provided.
  - The checkbox for "For others" should be marked with a cross and the name and address of the partnership should be indicated in the box provided.
4. In the field for "Country", please refer to the standard list of country codes made available by the Registry of Patents and enter the country code corresponding to the country in question.
5. The declaration of priority in paragraph 4 should state the date of the previous filing, the country in which it was made, and indicate the file number, if available. Where the application relied upon in an International Application or a regional patent application e.g. European patent application, one of the countries designated in that application [being one falling under section 17 of the Patents Act] should be identified and the country should be entered in the space provided.
6. Where the applicant or applicants is/are the sole inventor or the joint inventors, paragraph 5 should be completed by marking with a cross the 'YES' checkbox in the declaration (A) and the 'NO' checkbox in the alternative statement (B). Where this is not the case, the 'NO' checkbox in declaration (A) should be marked with a cross and a statement will be required to be filed on Patents Form 8.
7. When an application is made by virtue of section 20(3), 26(6) or 47(4), the appropriate section should be identified in paragraph 6 and the number of the earlier application or any patent granted thereon identified. Applicants proceeding under section 26(6) should identify which provision in rule 27 they are proceeding under. If the applicants are proceeding under rule 27(1)(a), they should also indicate the date on which the earlier application was amended.
8. Where the applicant wishes an earlier disclosure of the invention by him at an International Exhibition to be disregarded in accordance with section 14(4)(c), then the 'YES' checkbox at paragraph 7 should be marked with a cross. Otherwise, the 'NO' checkbox should be marked with a cross.
9. Where in disclosing the invention the application refers to one or more micro-organisms deposited with a depository authority under the Budapest Treaty, then the 'YES' checkbox at paragraph 8 should be marked with a cross. Otherwise, the 'NO' checkbox should be marked with a cross. Attention is also drawn to the Fourth Schedule of the Patents Rules.
10. Where an agent is appointed, the fields for "DETAILS OF AGENT" and "ADDRESS FOR SERVICE IN SINGAPORE" should be completed and they should be the same as those found in the corresponding Patents Form 41. In the event where no agent is appointed, the field for "ADDRESS FOR SERVICE IN SINGAPORE" should be completed, leaving the field for "DETAILS OF AGENT" blank.
11. In the event where an individual is appointed as an agent, the sub-field "Name" under "DETAILS OF AGENT" must be completed by entering the full name of the individual. The sub-field "Firm" may be left blank. In the event where a partnership/body corporate is appointed as an agent, the sub-field "Firm" under "DETAILS OF AGENT" must be completed by entering the name of the partnership/body corporate. The sub-field "Name" may be left blank.
12. Attention is drawn to sections 104 and 105 of the Patents Act, rules 90 and 105 of the Patents Rules, and the Patents (Patent Agents) Rules 2001.
13. Applicants resident in Singapore are reminded that if the Registry of Patents considers that an application contains information the publication of which might be prejudicial to the defence of Singapore or the safety of the public, it may prohibit or restrict its publication or communication. Any person resident in Singapore and wishing to apply for patent protection in other countries must first obtain permission from the Singapore Registry of Patents unless they have already applied for a patent for the same invention in Singapore. In the latter case, no application should be made overseas until at least 2 months after the application has been filed in Singapore, and unless no directions had been issued under section 33 by the Registrar or such directions have been revoked. Attention is drawn to sections 33 and 34 of the Patents Act.
14. If the space provided in the patents form is not enough, the additional information should be entered in the relevant continuation sheet. Please note that the continuation sheets need not be filed with the Registry of Patents if they are not used.

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# PREPARATION METHOD

The invention pertains to a method of preparing styrene or substituted styrene comprising (1) converting a mixture comprising alkylbenzene hydroperoxide or substituted alkylbenzene hydroperoxide to a mixture comprising phenyl alkanol or substituted phenyl alkanol and (2) dehydrating the phenyl alkanol or substituted phenyl alkanol

A commonly known process in which phenyl alkanol is converted with the help of a catalyst is a process in which propylene oxide and styrene are produced starting from ethylbenzene. In general such process involves the steps of (i) reacting ethylbenzene with oxygen or air to form ethylbenzene hydroperoxide, (ii) reacting the ethylbenzene hydroperoxide thus obtained with propene in the presence of an epoxidation catalyst to yield propylene oxide and 1-phenyl ethanol, and (iii) converting the 1-phenyl ethanol into styrene by dehydration using a suitable dehydration catalyst. Suitable processes are described for example in US 5,210,354. According to this process in both reaction steps (ii) and (iii) a homogenous catalyst was used. A homogeneous molybdenum catalyst was used for step (ii) and homogeneous p-toluene sulfonic acid was used for step (iii). It was found that the preparation of 1-phenyl ethanol led to the presence of heavy by-products in the crude 1-phenylethanol stream. The crude 1-phenylethanol stream was therefore subjected to a distillation step before step (iii). Feed to step (iii) was removed as an

overhead product and a heavy ends stream, containing some styrene precursors, was removed as a bottom product. US 5,210,354 further describes a process for treating this heavy ends stream to recover some styrene precursors.

In JP 8133995 a homogeneous molybdenum catalyst was used for performing step (ii). The advantage claimed for the process described is that the crude 1-phenylethanol stream is not distilled before being fed to step (iii). However, in order to make the stream suitable as feed for step (iii) the stream had to be treated by a caustic water wash at 30 to 180°C and water washing. This, however, is also an expensive and laborious method.

In European application 02252618.0 (not prepublished, our TS 1112), a process is described where a heterogeneous catalyst is used for step (iii). In the epoxidation step (ii) a homogeneous catalyst or a heterogeneous catalyst can be applied.

It is an objective of the present invention to obtain a method for which no need exists to treat the crude aryl alcohol feed to step (iii) by distilling off the heavy bottoms, or to wash these from the product. Such process would give a substantial commercial benefit over the prior art methods that need expensive distillation or washing steps. It is further of an additional advantage not to separate heavies as waste, since this heavy end stream contains valuable styrene precursors. Thus by using a process without distillation or washing the heavy bottoms, a further increase of the yield of valuable products is obtained.

Therefore, the present invention now relates to a process of preparing styrene or substituted styrene comprising (1) converting a mixture comprising

alkylbenzene hydroperoxide or substituted alkylbenzene hydroperoxide to a mixture comprising phenyl alkanol or substituted phenyl alkanol by oxidizing an alkene to an alkylene oxide in the presence of a heterogenous catalyst and (2) reacting the phenyl alkanol or substituted phenyl alkanol product of step (1) to obtain styrene or substituted styrene in the presence of a homogeneous dehydration catalyst. More specifically, the process includes a method of preparing a mixture comprising propylene oxide and 1-phenylethanol (also known as alpha-phenyl ethanol or methyl phenyl carbinol) or substituted 1-phenyl ethanol and subsequently dehydrating 1-phenylethanol or substituted 1-phenylethanol to styrene or a substituted styrene

In a preferred embodiment the method comprises oxidizing ethylbenzene and reacting the resulting mixture containing ethylbenzene hydroperoxide with propene in (1) using a heterogeneous catalyst to obtain a mixture comprising propylene oxide and 1-phenylethanol.

Heterogenous catalysts can be selected from catalysts containing titanium, zirconium, molybdenum and/or vanadium compounds. Catalysts containing titanium and/or zirconium and silica, are preferred. A particularly suitable heterogenous catalyst is catalyst containing titanium and silica, more specifically a catalyst as described in EP-A-345856.

Conditions under which epoxidation is carried out are known in the art and include temperatures of 75 to 150 °C and pressures up to 80 bar. The reaction medium is preferably in the liquid phase.

After the epoxidation step, unreacted propene, propylene oxide product and ethyl benzene solvent are separated from the crude 1-phenylethanol stream. The

crude phenylethanol stream is fed directly to the second, dehydration, step. This reaction is performed in the presence of a homogeneous catalyst. Preferred homogeneous catalysts are inorganic or organic acids, such as p-toluene sulfonic acid. According to the present process it is no longer required to subject the effluent from the epoxidation step (1) to a separation treatment to remove heavy components before feeding the crude 1-phenylethanol stream to the dehydration step (2). Heavy components which are especially preferred to be present, are compounds having a molecular weight of 195 or higher, more specifically 200 or higher. It was found that the presence of these heavy compounds resulted in the preparation of a relatively large amount of styrene or substituted styrene, based on amount of starting compounds used in the process.

The invention is further illustrated by the following examples.

Example 1

In a reactor, air was blown through ethylbenzene. The product contained ethylbenzene hydroperoxide.

The product obtained was reacted with propene in the presence of a heterogeneous titanium on silica catalyst as described in the Example according to EP-A-345856. Unconverted ethylbenzene and propylene oxide were removed from the product, and a crude 1-phenylethanol feed was obtained. This crude 1-phenylethanol stream had the following composition:

1-phenylethanol	77.6 wt.%
2-phenylethanol	3.5 wt.%
acetophenone	11.8 wt.%
2,3-diphenylethyl ether	0.7 wt.%
Other heavy components with boiling points above 2,3-diphenylethyl ether	1.3 wt.%

p-Toluene sulfonic acid was added to the crude 1-phenylethanol stream at a level of 200 ppmw (parts per million weight), and dehydration was carried out continuously in the liquid phase at 218 °C, 0.2 bar and at a throughput of 0.34 (g feed)/(g reaction liquid)/h. Crude styrene and water products were removed as vapour and condensed. The styrene concentration in product was determined by gas chromatography. The amount of heavy residue produced was 4.4 wt.% on styrene produced.

#### Example 2

A crude 1-phenylethanol stream was prepared as in Example 1. This was further treated by distillation, according to European application 02252618.0 (our TS 1112), so that the majority of heavy compounds were removed. The resulting stream had the following composition:

1-phenylethanol	80.9 wt.%
2-phenylethanol	3.7 wt.%
acetophenone	9.8 wt.%
2,3-diphenylethyl ether	0.02 wt.%
Other heavy components with boiling points above 2,3-diphenylethyl ether	not detected

p-Toluene sulfonic acid was added to the crude 1-phenylethanol stream at a level of 200 ppmw, and

dehydration was carried out continuously in the liquid phase at 218 °C, 0.2 bar and at a throughput of 0.39 (g feed)/(g reaction liquid)/h. Crude styrene and water products were removed as vapour and condensed. The styrene concentration in the product was determined by gas chromatography. The amount of heavy residue produced was 3.0 wt.% on styrene produced. The total of this heavy residue plus the heavy residue removed in the prior distillation step (0.7 wt.% of 2,3-diphenylethyl ether and 1.3 wt.% of other heavy components with boiling points above 2,3-diphenylethyl ether) exceeded the total heavy residue formed in Example 1.

#### Example 3

The crude 1-phenylethanol stream from Example 1 was treated as follows: p-toluene sulfonic acid was added to the crude 1-phenylethanol stream at a level of 200 ppmw, and dehydration was carried out continuously in the liquid phase at 238 °C, 0.2 bar and at a throughput of 0.19 (g feed)/((g reaction liquid).h). Crude styrene and water products were removed as vapour and condensed. The styrene concentration in the product was determined by gas chromatography. The amount of heavy residue produced was 2.3 wt.% on styrene produced.

#### Example 4

The distilled 1-phenylethanol stream from Example 2 was treated as follows: p-Toluene sulfonic acid was added to the crude 1-phenylethanol stream at a level of 200 ppmw, and dehydration was carried out continuously in the liquid phase at 239 °C, 0.2 bar and at a throughput of 0.31 (g feed)/(g reaction liquid)/h. Crude styrene and water products were removed as vapour and condensed. The styrene concentration in the product was determined by gas chromatography. The amount of heavy residue produced

was 1.6 wt.% on styrene produced. The total of this heavy residue plus the heavy residue removed in the prior distillation step (0.7 wt.% of 2,3-diphenylethyl ether and 1.3 wt.% of other heavy components with boiling points above 2,3-diphenylethyl ether) exceeded the total heavy residue formed in Example 3.

C L A I M S

1. A method of preparing styrene or substituted styrene comprising (1) converting a mixture comprising alkylbenzene hydroperoxide or substituted alkylbenzene hydroperoxide to a mixture comprising phenyl alkanol or substituted phenyl alkanol and (2) dehydrating the phenyl alkanol or substituted phenyl alkanol, characterized by oxidizing an alkene to an alkylene oxide in step (1) in the presence of a heterogenous catalyst and dehydrating the phenyl alkanol or substituted phenyl alkanol in step (2) in the presence of a homogenous dehydration catalyst to obtain styrene or substituted styrene.
2. The method according to claim 1, which is preceded by a non-catalyzed step wherein alkylbenzene or substituted alkylbenzene is oxidized to a mixture comprising alkylbenzene hydroperoxide or substituted alkylbenzene hydroperoxide.
3. The method according to claim 1 or 2 wherein in step (1) ethylbenzene hydroperoxide is converted to 1-phenylethanol, which in step (2) is converted to styrene.
4. The method according to any one of claims 1 to 3 wherein the heterogenous catalysts of step (1) is selected from supported titanium, zirconium, molybdenum, and vanadium compounds, and the homogenous catalyst of step (2) is selected from inorganic and organic acids.

5. The method according to any one of claims 1-4 wherein the heterogeneous catalyst contains titanium and silica, and the homogeneous catalyst is an aromatic and/or aliphatic sulfonic acid.



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PREPARATION METHOD

The invention pertains to a method of preparing styrene or substituted styrene comprising (1) converting a mixture comprising alkylbenzene hydroperoxide or substituted alkylbenzene hydroperoxide to a mixture comprising phenyl alkanol or substituted phenyl alkanol and (2) dehydrating the phenyl alkanol or substituted phenyl alkanol, characterized by oxidizing an alkene to an alkylene oxide in step (1) in the presence of a heterogenous catalyst and dehydrating the phenyl alkanol or substituted phenyl alkanol in step (2) in the presence of a homogenous dehydration catalyst to obtain styrene or substituted styrene.